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Variation of Gelatin Amount as Template for Mesoporous Silica-Alumina Synthesis based on Lapindo Mud

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The synthesis of mesoporous silica-alumina from Na_2SiO_3 and $NaAlO_2$ solutions extracted from lapindo mud using mesoporous gelatin templates from catfish bone extract has been performed. Mesoporous silica-alumina (MSA) synthesis was carried out by sol-gel method with a gelatin template of catfish bone for as much as 0.0; 0.5; 1.0 and 1.5 g, which produced MSA-G00, MSA-G05, MSA-G10 and MSA-G15, respectively. The obtained MSA was analyzed using FTIR, XRD, TEM and surface area analyzer (BET and BJH methods). The MSA-G00, MSA-G05, MSA-G10 and MSA-G15 showed a specific surface areas of 24.58, 41.73, 59.73, 89.82 m^2/g and pore diameters of 10.20, 3.86, 9.97, and 7.31 nm, respectively. The XRD results proved that all the MSA were amorphous while the TEM analysis showed that all prepared MSAs using gelatin as a template were wormhole-like pores.

Keywords: Mesoporous Silica-alumina, Gelatin, Lapindo mud.

INTRODUCTION

Mesoporous material is widely studied because it can be applied as a catalyst and catalyst support [1,2]. A catalyst support material must have a high surface area, adequate productivity, acid or base sites, and tolerance to temperature rise without being degraded [2]. Mesoporous silica-alumina is one of the mesoporous materials, which is extensively use in the industrial organic solvent and act as highly potential acid catalyst [2].

Lapindo mud is effectly use in the oil and gas exploration activities by PT Lapindo Brantas Inc. since 2006 and has submerged around 250 hacters of land in Sidoarjo, East Java [3]. The main ingredients of Lapindo mud are Al_2O_3, SiO_2, CaO, TiO_2 and Fe_2O_3 [4]. Lapindo mud flow reaches around 180,000 m^3 per day and contains a lot of silica and alumina materials. Therefore, these natural materials have the potential to be used as a mesoporous synthetic material [5]. Alumina leaching from the framework can be done by using strong acids [6] and to dissolve silica from the framework, a strong base can be used [7]. Alumina leaching using strong acids provides several advantages one of which is the low soluble silica [8]. The use of strong bases in the treatment of solids containing silica-alumina causes the dissolution of some silica from their structures due to extraction [9]. The synthesis of silica-alumina needs silicate and aluminate solutions so that the solution from the silica and alumina leaching from Lapindo mud can be used.

Surfactants are commonly used as templating materials to obtain the mesoporous materials with high surface areas, tunable pore sizes, large pore volumes and rich morphology. Various types of ionic and non-ionic surfactants have been employed for obtaining porous silica with different pore sizes and morphological characteristics [10]. Consequently, researchers have proposed various methods for synthesizing high-surface-area mesoporous materials *e.g.*, using porous carbon as a hard template, surfactants as a soft template, glucose as template, co-template of CTAB and tartaric acid, evaporation-induced self-assembly (EISA) [11], chitosan as template [12] and gelatin as template [5,12-14].

Gelatin is defined as partially hydrolyzed collagen in which the basic unit comprises a protein chain of about 1050 amino acids. The conversion of collagen into gelatin requires breaking hydrogen bonds, stabilizing the triple helix, and determining the random configuration of gelatin [14]. Gelatin is an important functional biopolymer that has a broad applications for food,

material, pharmacy and photography industries. Another useful application of gelatin is applied as a template for mesoporous silica. General template used for mesoporous material is an ammonium quartener type surfactant. However, this surfactant is hard to degrade by environment and may cause water eutrophication and environmental pollution. In order to avoid these disadvantages, some natural polymers have attracted researchers' considerable attention [12].

It is important to emphasize that the functional groups in gelatin may act as an excellent complexing agent of metallic cations such as Al^{3+} or Si^{4+}, which is very interesting during the synthesis of metal oxide catalysts with high metallic dispersion and porosity [14]. The most available gelatin is made from mammalian resources such as pork skins, cow bones and cow skin. However, other sources of gelatin are also becoming increasingly relevant such as catfish bones, scales and skin [15].

One of the methods for obtaining mesoporous material is the conventional sol-gel using various types of templates including urea [2], carboxylic acid [16], oxalic acid dihydrate [17] and pork gelatin [14]. The sol-gel method is a promising method and controls the process of hydrolysis and condensation to obtain the desired pore. Gelatin is used as a template for mesoporous silica synthesis [4,18] and in mesoporous silica-alumina synthesis [14,19]. Several studies have been conducted in investigating mesoporous silica synthesis with SiO_2 from Lapindo mud [3,4] as well as the synthesis of mesoporous silica-alumina using silicate and aluminate solids from Lapindo mud extraction [5,13,19].

This research was carried out by extracting sodium aluminate and sodium silicate from Lapindo mud as mesoporous silica-alumina (MSA) synthetic material. Gelatin extracted from catfish bone is used as MSA synthetic template, which was synthesized by sol-gel method with variations in the amount of gelatin to determine its effect on character and porosity

EXPERIMENTAL

The materials used in this research were Lapindo mud collected from Sidoarjo Regency, East Java and catfish bone from Pakem Sleman, Yogyakarta, Indonesia.

Silicate and aluminate extraction from Lapindo mud: Dried Lapindo mud (100 g) was sieved at 100 mesh and refluxed with 400 mL of HCl 6 M at 90 ºC for 5 h and then filtered. The filtrate was added NaOH till pH attained pH 13 and filtered again. The residue from reflux with HCl was dried and refluxed with 400 mL of 6 M NaOH at 90 ºC for 5 h and again filtered. Sodium aluminate and sodium silicate were analyzed for Al and Si content using atomic absorption spectrophotometer (AAS-PinAAcle 900T Perkin-Elmer).

Gelatin extraction from catfish bones: About 100 g of catfish bone was cleaned, dried and then soaked with 500 mL NaOH (1 M) for 24 h and finally washed with distilled water to neutral pH. It was then soaked using 250 mL of 0.8 M HCl for 30 min twice. The bone was then washed using distilled water to a pH of 5. The bone was also refluxed using 500 mL of steriled water at 70 ºC for 5 h and filtered. The filtrate was dried in an oven at 50 ºC. Gelatin was analyzed using FTIR (Shimadzu Prestige-21) and sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE, Mini Protein II Bio-Rad Laboratories Inc., Richmond, CSA, USA).

Synthesis of mesoporous silica-alumina (MSA): Synthesis of mesoporous silica-alumina was carried out using the sol-gel method by mixing 50 mL of $NaSiO_3$ solution with 50 mL of $NaAlO_2$ solution from Lapindo mud extract and the solution was adjusted to pH 8. Then, it was added with 50 mL solution containing 0; 0.5; 1.0 and 1.5 g of gelatin (here in after referred to as MSA-G00, MSA-G05, MSA-G10 and MSA-G15) while stirring vigorously. This mixture was then heated at 60 ºC for 4 h, while stirring vigorously and aging for 24 h. The mixture was filtered and the silica-alumina solids were calcined at 500 ºC and analyzed with FTIR (Shimadzu Prestige-21), surface area analyzer (SAA Quantachrome 1200e) and transmission electron microscope (TEM, JEOL JEM-1400).

RESULTS AND DISCUSSION

Silicate and aluminate extraction from Lapindo mud: The XRF results show that the Lapindo mud contains high contents of Si, Al and Fe as 48.61, 22.50 and 22.2%, respectively. Thus, to obtain a silicate and alumina solution it is necessary to extract the silicate and its aluminate [20]. The leaching with HCl acid causes the first Si-Al bonding of the aluminosilicate broken. Al_2O_3 allows dissolution in acids except SiO_2. In this case, silica and alumina can be separated by screening. Thus, Al_2O_3 is concentrated in the filtrate and SiO_2 as residue [21,22].

$$Al_2Si_2O_5(OH)_4 + 6\,HCl \rightleftharpoons 2AlCl_3 + 2SiO_2 + 5H_2O \quad (1)$$

$$AlO(OH) + 6HCl \rightleftharpoons 2AlCl_3 + 4H_2O \quad (2)$$

$$Fe_2O_3 + 6HCl \rightleftharpoons 2FeCl_3 + 3H_2O \quad (3)$$

Metal impurities were removed from the solution by the addition of 6 M NaOH at pH 13. The metal contents would be precipitated while sodium aluminate remains in solution form [22]. The reactions are as follows:

$$AlCl_3 + 4NaOH \rightleftharpoons NaAlO_2(OH) + 3NaCl \quad (4)$$

$$FeCl_3 + NaOH \rightleftharpoons Fe(OH)_3\downarrow + NaCl \quad (5)$$

Solid residues of alumina extract after being washed and dried were then refluxed using 6M NaOH. In this process, the reaction takes place according to the following reactions [22,23]:

$$SiO_2 + NaOH \rightleftharpoons Na_2SiO_3 + H_2O \quad (6)$$

Table-1 shows that total Al content in the sodium silicate yield was 25,872.701 mg/L, which indicate that HCl is effective in the Al leaching process of Lapindo mud. Meanwhile, extraction with NaOH shows that the extracted Si content is 172,744.858 mg/L. These results indicate that NaOH base can

TABLE-1
AAS ANALYSIS RESULTS ON SODIUM ALUMINATE AND SODIUM SILICATE

Material	Content (mg/L)		
	Si	Al	Fe
Sodium-aluminate	30.870	25,872.701	0.937
Sodium-silicate	172,744.858	1,426.054	4.206

extract silica well. The content of Fe in sodium aluminate and sodium silicate is relatively low at 0.937 and 4.206 mg/L, respectively.

Gelatin extraction from catfish bones: Gelatin is a polypeptide resulting from collagen hydrolysis produced from the skin, connective tissue and bone [15,24]. Gelatin extraction from fish bones can be performed using alkalis or acids or with the combination of both followed by the hydrolysis process [12,13,25,26]. Gelatin extraction from catfish bones using pretreatment was done by soaking in 0.1 M NaOH solution and 0.8 M HCl followed by refluxing at 70 ºC for 5 h with a yield of 5% and molecular weight 20-150 kDa. The FTIR spectrum in Fig. 1 shows that gelatin produced from catfish bones containing amide-A is characterized by the appearance of a peak at 3487 cm^{-1}, which is a combination with stretch CH_2 in carboxylic acids in a stable dimeric associated state [27,28]. Amide B band appears at 2931 cm^{-1} in which amide B of collagen exhibits [29]. Amide I is shown by the absorption band at ~1651 cm^{-1} corresponding to -C=O strain vibration. Amide II is shown by the absorption band at 1543 cm^{-1}, which shows -NH buckling vibration joining the stretch -CH while amide III is shown by absorption band 1064 cm^{-1}, which is related to bending -NH [30].

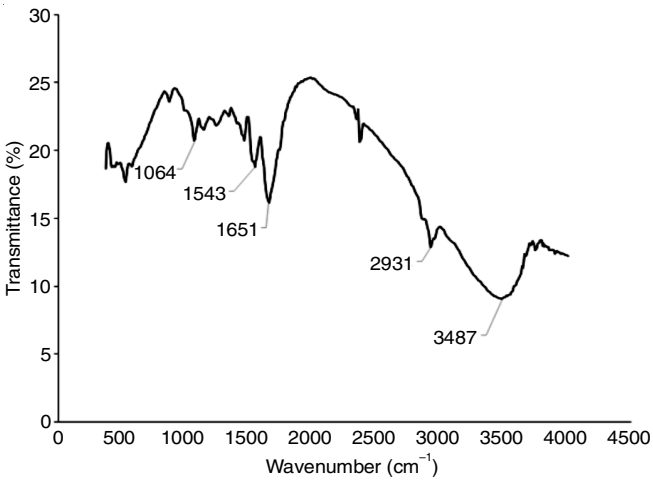

Fig. 1. FT-IR spectra of gelatin extracted from catfish bones

FTIR analysis of mesoporous silica alumina (MSA): The structure of MSA-G00, MSA-G05, MSA-G10 and MSA-G15 synthesis was analyzed using FTIR technique. Fig. 2 shows all absorption in the range of 1000-600 cm^{-1} indicate the bending vibration absorption band and silica-alumina vibration [31]. The absorption band at around 1057 cm^{-1} attributed the T-O-T asymmetric stretching band (T=Si and /or Al), around 779 cm^{-1} is due to the T-O-T asymmetric stretching band in the field of bending mode, and at the band at 471 cm^{-1} is due to the T-O-T vibration absorption [32].

Porosity analysis using surface area analyzer of synthesized MSA is shown in Table-2. The measurements with surface area analyzer on alumina silica synthesized using a gelatin template show the differences compared to the results of synthesis without gelatin. The BJH analysis results of MSA desorption with gelatin templates have lower pore diameters compared

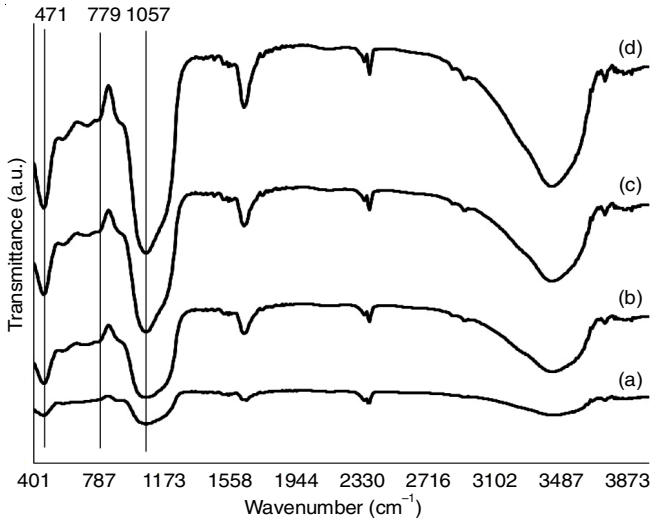

Fig. 2. FTIR spectra of: (a) MSA-G00 (b) MSA-G05 (c) MSA-G10 (d) MSA-G15

TABLE-2
MESOPOROUS SILICA-ALUMINA POROSITY ANALYSIS WITH SURFACE AREA ANALYZER

	MSA-G00	MSA-G05	MSA-G10	MSA-G15
Pore diameter (nm)[a]	10.20	3.86	9.97	7.31
Surface area (m^2/g)[b]	24.58	41.73	59.73	89.82
Pore volume (cm^3/g)[c]	0.10	0.09	0.16	0.28

[a]BJH desorption method; [b]BET method; [c]Pore volume determined by nitrogen gas.

to MSA without gelatin. However, all the synthesized MSA have a pore diameter ranged from 2 to 50 nm. This shows that gelatin plays an effective role as an agent of forming mesoporous structures [18] in a mixture of sodium silicate and sodium aluminate as a result of Lapindo mud extraction. In this study, the pore diameter without gelatin (MSA-G00) had a quite large pore of 10.20 nm, while MSA-G05 decreased the pore diameter to 3.86 nm. In MSA-G10 and MSA-G15 samples, the pores increased to 9.97 and 7.31 nm. The amount of gelatin can cause a difference in pore diameter to a certain degree but it will not cause other significant pore changes [18]. The amount of gelatin added also results in a significant increase in pore and outer surface in which there is a three-fold difference in surface area between MSA-G00 and MSA-G15. At low gelatin concentration, there was a synergistic effect between gelatin and silica in which negatively charged silica induces an aggregation of positively charged gelatin forming a gel network that directs the growth of particles [33]. Thus, gelatin is trapped between silica tissue and plays the role of a template, leaving pores after extraction [18].

The isotherm patterns of synthesized MSAs (Fig. 3) exhibited a type IV which is a mesoporous adsorbent according to IUPAC. The adsorption behaviour in mesoporous was determined by the adsorbent-adsorptive interaction and also by the interaction between the molecules in a condensed state [34]. Overall, MSA has a coincident tendency at relative pressure of N_2 below $p/p_o < 0.5$. A moderate increase in N_2 adsorption occurred at around 0.5 then progressively increases at higher relative press-

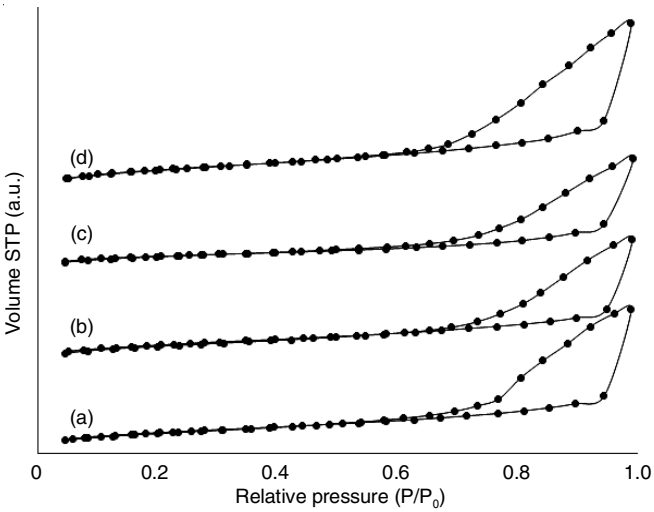

Fig. 3. Nitrogen gas adsorption-desorption isotherm of: (a) MSA-G00 (b) MSA-G05 (c) MSA-G10 (d) MSA-G15

ures indicating the mesoporosity in the synthesized MSAs [35]. This form of hysteresis involves a vapor percolation threshold from a boundary curve that occurs at p/p_o value of around 0.5, which reflects a steep evaporation curve from the pores presenting steric resistance in which the interphase becomes mechanically unstable. This sudden evaporation of the pores also called the cavitation phenomenon, which consists of nucleating the bubbles in a thick phase like liquid. It allows the sudden release of almost all of these last phases into the bulk vapors surrounding the sample [18].

Fig. 4 shows the XRD spectra of the MSA-G00, MSA-G05, MSA-G10 and MSA-G15, which are one type of spectra with other 2θ at 20º to 30º signifying that MSA is amorphous material. As indicated earlier [20,36], TEM analysis of MSA-G00, MSA-G05, MSA-G10 and MSA-G15 (Fig. 5) show that

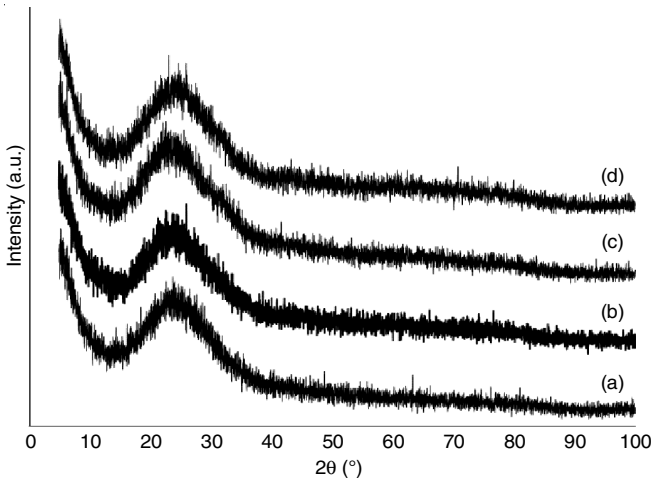

Fig. 4. Diffractograms of: (a) MSA-G00 (b) MSA-G05 (c) MSA-G10 (d) MSA-G15

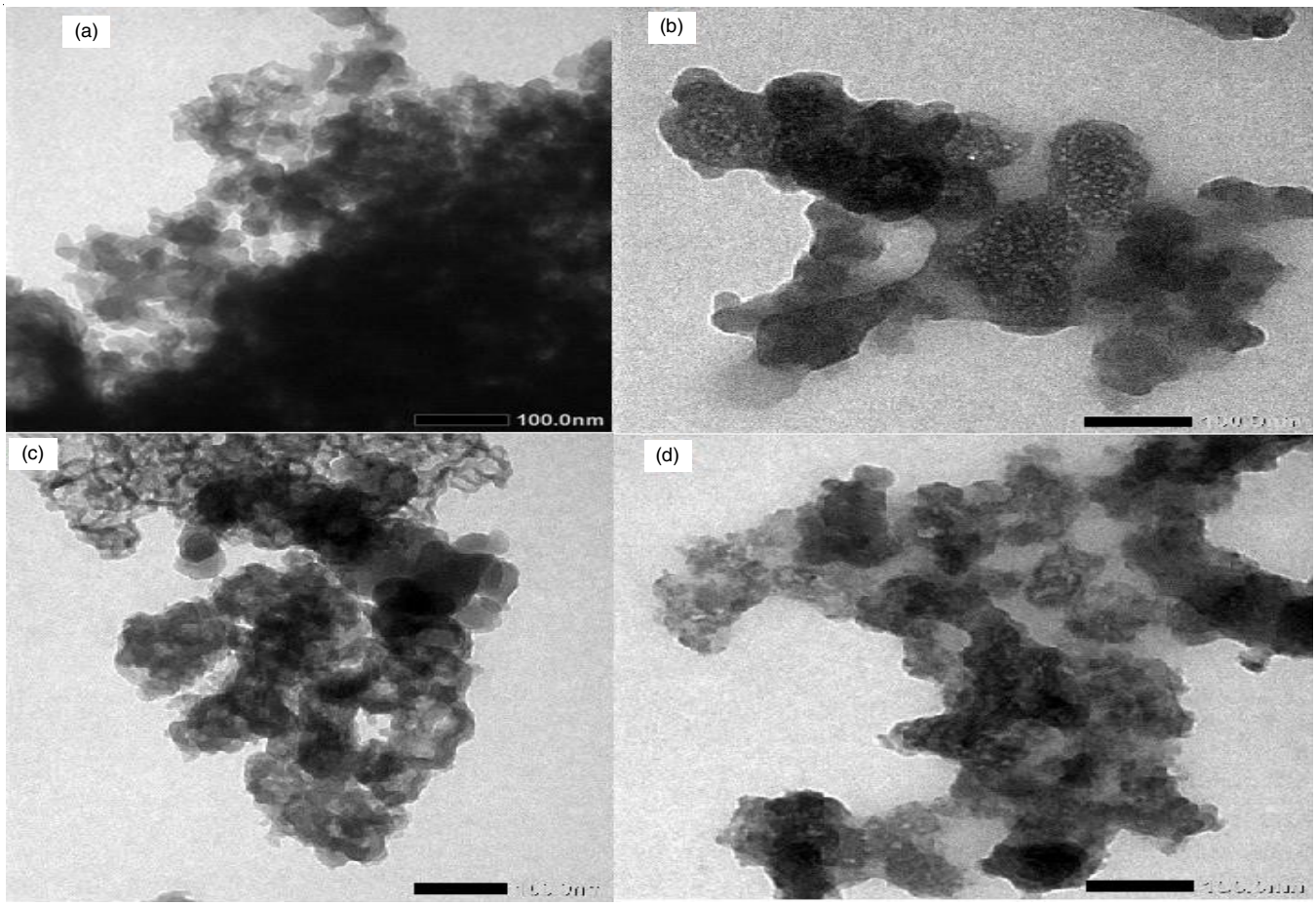

Fig. 5. TEM image of: (a) MSA-G00 (b) MSA-G05 (c) MSA-G10 (d) MSA-G15

MSA-G00 tends to have agglomerated particles with more regular pores whereas MSA-G05, MSA-G10 and MSA-G15 have pores like holes worms. In this case, the greater the concentration of gelatin is, the formed worm holes are getting more and more so that the resulting surface area is higher. This is related to the increase in MSA surface area while amount of gelatin also increases.

Conclusion

Synthesis of mesoporous silica-alumina from $NaSiO_3$ and $NaAlO_2$ from Lapindo mud extraction was successfully carried out. The presence of gelatin templates from catfish bones raises the surface area significantly compared to the absence of gelatin templates. The MSA-G00, MSA-G05, MSA-G10 and MSA-G15 show specific surface area of 24.58, 41.73, 59.73, 89.82 m^2/g and pore diameter of 10.20, 3.86, 9.97 and 7.31 nm, respectively. The XRD results proved that all mesoporous silica-alumina (MSAs) are amorphous in nature. The TEM analysis showed that all MSAs using gelatin as a template are wormholes like pores.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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